previously[1] reported, and this is the first report in which repetitive pulses have been used to consecutively release small amounts. Continuing work will explore the generality and details of release as well as develop specifically useful devices.

Acknowledgment. This work was supported by the National Institutes of Health.

Registry No. ClO_4^-, 14797-73-0; NaCl, 7647-14-5; Glu, 56-86-0; FCN, 13408-63-4; carbon, 7440-44-0; pyrrole, 109-97-7.

Dimethylsilanone Enolate

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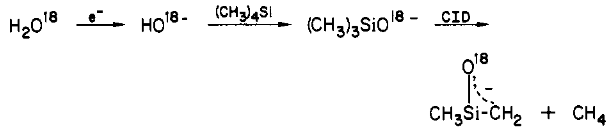
The widespread interest in compounds containing multiply bonded silicon is clearly illustrated in the current literature.[1-6] Numerous efforts to generate and characterize these elusive species have been described, culminating in the first stable silaethylene recently reported by Brook and co-workers.[7] Parallel efforts in the theoretical community have likewise provided a fascinating picture of silicon–oxygen, silicon–carbon, and silicon–silicon multiple bonds which has occasioned a lively debate concerning the relative stabilities of the corresponding silylene tautomers.[8-11] Among the more commonly studied examples of multiply bonded silicon–oxygen compounds is dimethylsilanone, $(CH_3)_2Si{=}O$.[12] This second-row analogue of acetone is frequently invoked as an intermediate in polysiloxane and silaoxetane pyrolysis[13] and was recently identified in a low-temperature matrix as a reaction product from dimethylsilylene and N_2O.[14]

We describe here the formation and reactivity of the enolate ion of dimethylsilanone (**1**), which has been generated in the gas phase by collision-induced dissociation (CID) of trimethylsiloxide anion. Ion–molecule reactions and consecutive CID experiments are described that illustrate marked differences in the chemistry of **1** relative to its carbon analogue, $CH_3COCH_2^-$.

All experiments were carried out with a prototype Nicolet FTMS-1000 described previously.[15] Trimethylsiloxide anion, $(CH_3)_3SiO^-$, is initially formed by the DePuy reaction between OH^- and tetramethylsilane.[16] Following a 1.0-s interval to permit buildup of ion intensity, a 7.35-V, 0.1-ms resonant CID pulse is applied to $(CH_3)_3SiO^-$, and a 35-ms delay is allowed for its collisional dissociation against argon at ca. 5×10^{-6} torr.[17] A single daughter fragment ion is produced (*m/z* 73), which is shown to be due solely to methane loss by exclusive production of an *m/z* 75 daughter ion, **2**, when the in situ ^{18}O-labeled trimethylsiloxide ion is dissociated under identical conditions (eq 1).[18] This fragmentation pathway is analogous to methane loss from *tert*-butoxide ion which can be induced either by collisional activation[19] or photodissociation.[20] Application of a subsequent CID pulse to *m/z* 73 results in its further fragmentation via methyl cleavage to give CH_2SiO^- (*m/z* 58).



$$H_2O^{18} \xrightarrow{e^-} HO^{18-} \xrightarrow{(CH_3)_4Si} (CH_3)_3SiO^{18-} \xrightarrow{CID} CH_3Si(O^{18})CH_2^- + CH_4 \quad (1)$$

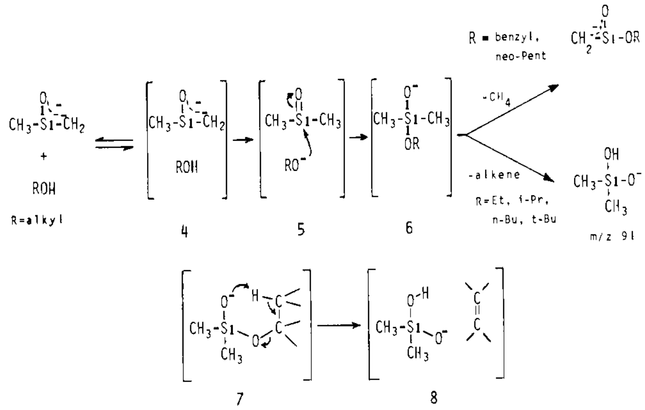
2

Table I. Reactions of Dimethylsilanone Enolate with Brønsted Acids

entry	ref acid	ΔH_{acid}[a]	proton transfer obsd?	other ions (*m/z*)[c]
a	CH_3OH	379.2	no	
b	CH_3OD		no	
c	CH_3CH_2OH	376.1	no	91
d	CH_3CH_2OD		no	92 (93)[b]
e	$(CH_3)_2CHOH$	374.1	no	91
f	$(CH_3)_2CHOD$		no	92 (93)[b]
g	$(CD_3)_2CDOD$		no	93
h	$CH_3CH_2CH_2CH_2OH$	374.0	no	91
i	$(CH_3)_3COH$	373.3	no	91
j	$(CH_3)_3CCH_2OH$	371.8	no	145
k	$C_6H_5CH_2OH$	369.6	no	165
l	$C_6H_5NH_2$	367.1	no	166
m	CF_3CH_2OH	364.4	yes	
n	CH_3SH	359.0	yes	

[a] kcal/mol; ref 24. [b] Secondary product ion derived from further reaction of *m/z* 92 with deuterated alcohol. [c] All reactant/product ion relationships confirmed by double resonance.

Scheme I



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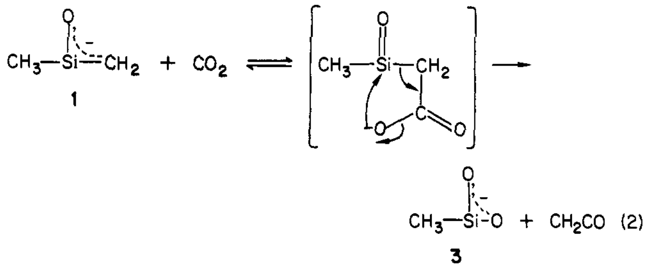
Ion **1** reacts with either CO_2 or SO_2 to give a single product ion at m/z 75. We formulate a structure for this product as the 2-silaacetate anion **3**, which can be derived by a metathesis mechanism reminiscent of the Wittig reaction[21] (eq 2). In



contrast, acetone enolate undergoes no reaction with either CO_2 or SO_2 under the low-pressure conditions of the FTMS and only slowly associates with CO_2 at higher pressure in a flowing afterglow.[22] As with **1**, $CH_3SiO_2^-$ also fragments by methyl cleavage when collisionally activated, in this case forming SiO_2^- (m/z 60).[23]

Reactions of **1** with a series of Brønsted acids have been examined in order to derive a quantitative measure of its basicity. From the observations summarized in Table I, we assign the proton affinity of **1** to be 366 ± 3 kcal/mol, which is slightly less than the measured value for acetone enolate of 368.8 kcal/mol.[24] This observation is consistent with the relative acidity enhancements noted for other α-silicon acids.[16,25]

Given that this proton affinity estimate is correct, we were surprised to discover that when **1** is allowed to react with either CH_3OD, CH_3CH_2OD, or $(CH_3)_2CHOD$, no H/D exchange occurs in the anion. This is in striking contrast to acetone enolate, which undergoes five rapid H/D exchanges in the presence of each of these reagents.[26] Consideration of the other ionic products from the alcohol reactions listed in Table I suggests a reason for the absence of exchange. Each of the alcohols bearing β-hydrogens yields a product ion at m/z 91 which shifts to m/z 92 in the case of CH_3CH_2OD and $(CH_3)_2CHOD$. Moreover, benzyl alcohol and neopentyl alcohol, which do not possess β-hydrogens, produce only products corresponding to addition with loss of methane. A unified mechanism that accounts for these results is shown in Scheme I. An endothermic proton transfer from alcohol to enolate initially occurs within the energy-rich collision complex (**4** → **5**). With carbon enolates and deuterated alcohols, this is a reversible process which leads to H/D exchange.[27] However, in the present case, the nascent alkoxide is *irreversibly* trapped by the formation of a strong silicon-oxygen bond[28] in adduct **6**. Subsequent decomposition of this intermediate occurs either by methane loss to give the observed silaester enolates (entries j and k, Table I) or by olefin cleavage to produce the silanone hydrate anion at m/z 91. We view this latter process as occurring via a cyclic elimination mechanism (**7** → **8**), similar to ester pyrolysis.[29] The results for the deuterated alcohols offer strong support for this hypothesis. $(CH_3)_2CHOD$ produces the carbon-deuterated silanone hydrate anion (m/z 92) which undergoes a single H/D exchange on oxygen in subsequent encounters with the deuterated alcohol. Furthermore, $(CD_3)_2CDOD$ initially produces only the dideuterated anion (m/z 93), which undergoes no further exchange.

The foregoing results illustrate the rich chemistry of dimethylsilanone enolate. The full details of these experiments as well as additional results for other unsaturated group 4 anions will appear in future publications.

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X-ray Absorption Spectroscopy of Nickel in the Hydrogenase from *Desulfovibrio gigas*

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Nickel has been identified as an integral component of hydrogenases from a number of different microorganisms, including *Chromatium vinosum*,[1] *Desulfovibrio gigas*,[2] and several *Methanobacterium* species.[3,4] All of these enzymes also contain one or more Fe–S clusters, and the *Methanobacterium thermoautotophicum* enzyme contains a flavin prosthetic group as well. Although the detailed nature of the active sites in these hydrogenases varies among sources, they are all characterized by electron paramagnetic resonance (EPR) signals assignable to a Ni(III) site in some form of the enzyme. There is also evidence for two of the hydrogenases exhibiting magnetic interaction between the Ni(III) site and one or more of the Fe–S clusters. In *D. gigas*, partial reoxidation of the H_2-reduced enzyme generates an EPR signal with $g' = 11.35$ (at X-band)[2] which is reminiscent of the "$g12$" signal observed in some oxidized forms of cytochrome *c* oxidase. In the latter case, this signal has been suggested to arise from coupling of two paramagnetic centers ($Fe_{a_3}^{3+}$ ($S = {}^5/_2$) and Cu_B^{2+} ($S = {}^1/_2$)) resulting in a non-Kramers system.[5]

We have initiated an X-ray absorption spectroscopic (XAS) study of the *Desulfovibrio gigas* enzyme. Our preliminary results reported here indicate that the nickel is reduced from Ni(III) to Ni(II) upon H_2 reduction of the oxidized enzyme and that the ligands are bound to the nickel through sulfur atoms.

The hydrogenase from *Desulfovibrio gigas* (grown on a medium described by LeGall et al.[6]) was purified by ion exchange chromatography as previously described[2] except that the crude extract was obtained by breaking the cells with use of a Gaulin Laboratory Homogenizer rather than with washing. The protein exhibited a single band on disc acrylamide gel electrophoresis.[7] Hyd-

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